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CERAMIC MATERIAL BASED ON ACID FLUORIDE

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A technology for producing a gypsum-ceramic material based on acid fluoride, which is an industrial chemical waste, is developed. The resulting material can be easily polished, does not accumulate static electricity, and has a surface texture resembling marble.

Acid fluoride is powdered waste generated by the Galogen Production Company in hydrofluoric acid manufacture. It contains more than 92% anhydrous calcium sulfate $CaSO_4$, and the rest is represented by calcium fluoride CaF_2 and calcium carbonate. The chemical composition of acid fluoride is as follows (wt.%): 35.0 – 36.5 CaO, 2.2 – 5.0 CaF_2, 2.6 – 3.4 SiO_2, 0.5 – 0.7 Al_2O_3, 0.2 – 0.95 Fe_2O_3, and the rest SO_3. Considering its chemical and mineralogical compositions, it appears cost-effective to use acid fluoride instead of natural anhydride in the mass production of materials based on calcium sulfate.

The production of gypsum ceramic materials based on gypsum-bearing waste generated in the production of phosphoric fertilizers suffers a drawback, i.e., substantial linear shrinkage of articles in firing [1]. The high (up to 15 – 30%) shrinkage is due to the chemical composition of gypsum-bearing waste containing calcium sulfate dihydrate. In firing, the crystal hydrate loses water, which is accompanied by fire shrinkage of articles. When acid fluoride is used as a source material in the production of gypsum ceramics, the deformation of articles is caused only by the liquid-phase sintering factor [2]; therefore it decreases 15 – 20 times. Furthermore, using various fluxes (sodium chloride, calcium chloride, sodium silicate solutions), it is possible to obtain good mechanical parameters and impart water resistance to gypsum-ceramic articles.

This study was based on powdered acid fluoride corresponding to standard TU 6-00-05807960-88–92. The granulometric composition of acid fluoride is listed in Table 1.

Thus, acid fluoride powder is mainly (73%) represented by small particles sized below 2.5 mm, among which particles below 1.25 mm prevail (over 62%).

The x-ray patterns of fluoride shows reflections due to insoluble anhydride β-$CaSO_4$ (d = 3.50, 2.85 Å), soluble anhydride γ-$CaSO_4$ (d = 2.80, 5.47 Å), fluorite CaF_2 (d = 3.15, 1.93, 1.65 Å), and calcite $CaCO_3$ (d = 3.03, 5.47 Å). There are also reflections of low intensity correlating to gypsum dihydrate $CaSO_4 \cdot 2H_2O$ (d = 4.27, 7.72 Å).

For the purpose of increasing the strength and water resistance of acid fluoride composites, the behavior of acid fluoride at high temperatures using fluxes was studied. This led to liquid-phase sintering of the composite with recrystallization of the initial composition [3].

The sintering temperature was determined experimentally. Its maximum temperature level was 900°C, since above that temperature anhydride started dissociating, releasing sulfur dioxide (Fig. 1). The optimum sintering temperature was 800°C.

To improve sintering of gypsum ceramics, acid fluoride was mixed with diluted waste water, which was an oil-field byproduct, to a molding moisture of 6 – 8%. The waste water constituted a 32% solution of mineral salts, among which the prevailing salt was sodium chloride NaCl (d = 2.83, 2.00, 1.41, 1.26 Å), with small quantities of calcium chloride $CaCl_2 \cdot 6H_2O$ (d = 3.26, 2.16, 1.70, 1.48 Å). The presence of sodium chloride makes it possible to neutralize the residual sulfuric acid in fluoride during sintering. In this process sodium sulfate is formed, which acts as a flux in firing.

TABLE 1

Sieve size, mm	Residue on the sieve, %	
	partial	total
20	0.7	0.7
10	1.9	2.6
5	6.6	9.2
2.5	18.0	27.2
1.25	10.0	37.2
0.63	18.8	56.0
0.315	11.6	67.6
0.14	26.0	93.4
< 0.14	6.6	100.0

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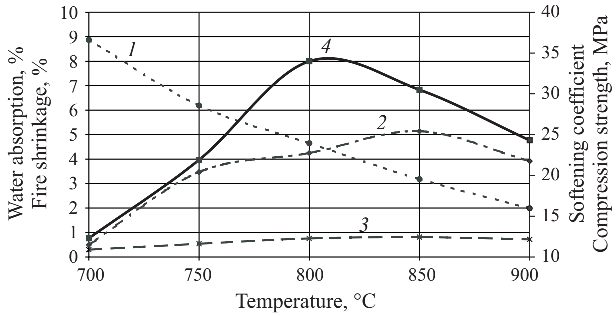

Fig. 1. Dependence of physicomechanical properties of gypsum-ceramic material on firing temperature: *1*) water absorption; *2*) fire shrinkage; *3*) softening coefficient; *4*) compression strength.

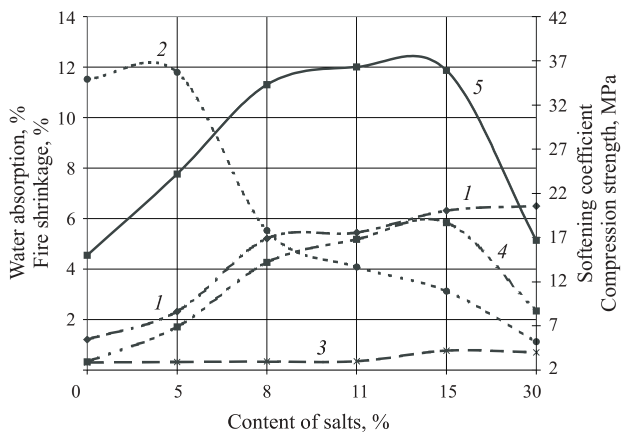

Fig. 2. Dependence of physicomechanical properties of gypsum-ceramic material on the content of salts in waste water: *1*) fire shrinkage; *2*) water absorption; *3*) softening coefficient; *4* and *5*) bending and compression strength, respectively.

Thus, the batch subjected to sintering contains anhydride $CaSO_4$, sodium chloride NaCl, sodium sulfate Na_2SO_4, and calcium chloride $CaCl_2$. This system in heating forms low-melting eutectics [4]. The thermogram of the fluoride composite shows the presence of calcium sulfate dihydrate (the endothermic effect at 170°C), and the first indication of melt occurs at temperatures of 560 – 580°C. Complete sintering with recrystallization of the composition ends at a temperature of 800°C. With further increase in the temperature, an endothermic effect is manifested (870°C), which is evidence of dissociation of anhydride to calcium oxide.

The physicomechanical properties of the material obtained upon variations of the salt content in the waste water are indicated in Fig. 2.

The optimum results were obtained with a 15% content of salt in the waste water, which is confirmed by stabilization of fire shrinkage and the optimum mechanical parameters [5]. The maximum value of the softening coefficient is ensured in this case.

An analysis of the microstructure of the gypsum-ceramic material using a Stereoscan S-200 scanning electron micro-

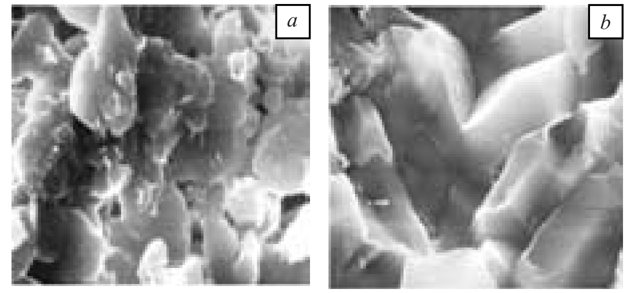

Fig. 3. The microstructure (× 3000) of gypsum ceramic composites prepared without adding waste water (*a*) and adding water containing 15% of salts (*b*).

Fig. 4. Microstructure of gypsum ceramic materials after storage in water.

scope established that when the batch is fired without adding waste water, the surface of the granules fuses with subsequent sintering into a porous conglomerate (Fig. 3*a*). When the batch is mixed with waste water, the structure acquires clearly defined crystallinity (Fig. 3*b*).

The x-ray phase analysis and the study of the microstructure (Fig. 4) of the gypsum ceramic material exposed in the conditions of increased moisture indicated the condensation of the structure of the sample by means of crystal hydrates based on gypsum dihydrate (d = 7.60, 4.27 Å) and an increase in strength by 15 – 25%.

The observed alterations suggest that acid fluoride can be used in the production of gypsum ceramics of increased strength and water resistance. The stability of properties of such materials is achieved by hydration of fluoride under the effect of moisture. The emerging crystal hydrates fill the pores and increase the density of the material structure.

Compared with similar materials obtained from gypsum-bearing waste, the considered material has significantly lower fire shrinkage. The use of oil-field waste water makes it possible to eliminate fluxes, which have complex compositions and, consequently are economically ineffective. The use of acid fluoride, which is industrial waste, improves the environmental situation on the territorories adjacent to dumping areas for fluoride-bearing waste.

The developed material can be easily ground and polished, does not accumulate static electricity, and has a surface texture resembling marble. Products based on this gypsum-ceramic material can be used for interior decoration and can replace artificial marble.

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